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SYNTHESIS, ELECTRICAL CONDUCTIVITY, AND MAGNETISM OF A NEW MOLE--ETC(U)
JUN 79 J T WROBLESKI, D B BROWN

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Synthesis, Electrical Conductivity, and Magnetism of a New Molecular Metal,
 $K_2[Ni(1,2-dithiooxalate)]_{2.11} \cdot 1.0$.

by

10 James T. Wrobleksi and David B. Brown

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Department of Chemistry

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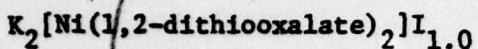
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Samples of K ₂ [Ni(DTO) ₂]I _{1.0} (DTO = 1,2-dithiooxalate) have been prepared by either solid-state oxidation of K ₂ [Ni(DTO) ₂] with excess I ₂ at 130–140°C or electrolysis of K ₂ [Ni(DTO) ₂] in methanol solution saturated with tetraethylammonium iodide. This material exhibits metal-like electrical conductivity ($\sigma^{300K} \approx 500 \Omega^{-1} cm^{-1}$) which, for one sample (sample A), persists to the lowest temperature at which data were obtained (20 K). Other samples of K ₂ [Ni(DTO) ₂]I _{1.0} undergo a metal-to-insulator transition at temperatures		

as high as 190 K. Variable-temperature (20-300 K) magnetic susceptibility data for sample A were obtained. The effective magnetic moment for sample A decreases from $2.4\mu_B$ at 295 K to $2.2\mu_B$ at 40 K. Below 40 K the value of μ_{eff} increases and becomes field dependent. A bonding model for this material is proposed.

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Synthesis, Electrical Conductivity, and Magnetism of a New Molecular Metal,



Sir:

Mixed-valence, linear-chain polymers which possess relatively high electrical conductivity have been prepared from square-planar ⁸ transition-metal complexes which contain C, N, O, or S donor groups. Examples of these highly-conducting compounds are $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ ¹ (C donor), $[Ni(phthalocyanine)](I_3)_{0.33}^2$ (N donor), $K_{1.81}[Pt(C_2O_4)_2] \cdot 2H_2O$ ³ (O donor), and $NH_4[Ni(mnt)_2] \cdot xH_2O$ ⁴ (S donor). Of these compounds, only $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ and $[Ni(phthalocyanine)](I_3)_{0.33}$ exhibit metal-like electrical conductivity ($\partial\sigma/\partial T < 0$). Although several organic donor-acceptor complexes which contain sulfur (TTF-TCNQ is an example)⁵ possess metal-like conductivity near room temperature, no transition-metal complex with an organic sulfur ligand has previously been reported to possess metal-like conductivity.⁶

As part of our overall effort to synthesize new, highly-conducting transition-metal complexes we have recently prepared samples of $K_2[Ni(DTO)_2]I_{1.0}$ (DTO = S, S' - 1,2-dithiooxalate dianion) which show metal-like conductivity in the temperature range 20-400 K. These samples were prepared by reacting three-times recrystallized $K_2[Ni(DTO)_2]$ ⁷ with a two-fold excess of I_2 in an evacuated, sealed glass tube for five days at 130-140°C. After this time the unreacted I_2 was removed under vacuum at 90°C. The copper-colored compound prepared in this manner reacts slowly with water if stored in air below 90°C. Chemical analysis⁸ of freshly-prepared samples were consistent with the formula $K_2[Ni(DTO)_2]I_{1.0 \pm 0.05}$. Although we have reproduced this preparation several times, these reaction conditions do not always produce a product with metallic conductivity. In fact, our success rate with this process has been three metal-like products in 24 attempted syntheses under (apparently) identical conditions. We have been unable to explain this marked irreproducibility. In the preparations which did not yield a product with metallic conductivity, I_2 uptake by $K_2[Ni(DTO)_2]$ occurs only

to the extent of 0.25 - 0.65 I per Ni. These "I deficient" products have room temperature electrical conductivities near $1 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$.

The electrical conductivity of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ is significantly higher than that which has been reported for other stacked transition-metal complexes, with compaction conductivities at room temperature on the order of $500 \Omega^{-1} \text{ cm}^{-1}$.

Figure 1 illustrates the temperature-dependence of the electrical conductivity of several samples of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$. These data were obtained by using pressure contacts on pressed pellet specimens. The four contacts were arranged in the van der Pauw configuration⁹ and supported in a specially-constructed low-temperature cell made of Teflon. Dc electrical conductivities were calculated from the following expression

$$\sigma(\Omega^{-1} \text{ cm}^{-1}) = 0.2206 \frac{\text{I}}{\text{tV}}$$

in which I is the applied current, V is the observed voltage drop across the sample, and t is the sample thickness in cm. All the metallic samples of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ displayed ohmic behavior under the experimental conditions (I = 10-90 mA). Data set A in Figure 1 was obtained with a freshly-prepared sample of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ powder which had been kept at 90°C prior to making the measurements. The conductivity of this sample increased slowly in the temperature range 373 to 250 K then increased more rapidly to 24 K. No metal-to-insulator transition was observed for this sample at $T \geq 24$ K. In contrast, the conductivity of sample B (Figure 1) maximizes near 190 K. Sample B was stored at room temperature in air for several days prior to making the measurements. Below 190 K the conductivity of sample B dropped rapidly to approximately $1\Omega^{-1} \text{ cm}^{-1}$ at 80 K. A low-temperature maximum in the conductivity vs. T curve was also observed for sample C (Figure 1). This sample was a compaction of small (< 100μ), copper-colored crystals of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}_{1.0}$. These crystals were obtained at a platinum anode by electrolysis (1.5 V) of a concentrated methanolic solution of $\text{K}_2[\text{Ni}(\text{DTO})_2]$ and tetraethylammonium iodide. This sample showed metal-like conductivity in the temperature range 300 to 90 K. At 90 K the conductivity of the sample began to decrease, reaching a value of $40 \Omega^{-1} \text{ cm}^{-1}$ at 22 K. We have as yet been unable to prepare single crystals of $\text{K}_2[\text{Ni}(\text{DTO})_2]\text{I}$ which are

large enough for single-crystal X-ray diffraction or for measurements of the anisotropy of conductivity.

Samples of $K_2[Ni(DTO)_2]I$ with metal-like conductivity are paramagnetic, as compared to highly-purified $K_2[Ni(DTO)_2]$ which is diamagnetic. The variable-temperature magnetic susceptibility and effective magnetic moment per Ni of highly-conducting sample A are shown in Figure 2. The value of μ_{eff}/Ni decreases from $2.6\mu_B$ at room temperature to approximately $2.2\mu_B$ at 40 K. Below 40 K the magnetic moment increases and becomes field dependent. This low-temperature behavior indicates the onset of ferromagnetic order in the material. In contrast to sample A, samples B and C behave as normal paramagnets over this entire temperature range ($\mu_{eff} \approx 2.4\mu_B$ at 300 K and $2.1\mu_B$ at 25 K.) We observe no magnetic anomaly for samples B and C in the vicinity of their metal-to-insulation transition temperatures (190 and 90 K, respectively.)

Although detailed analysis of the properties of $K_2[Ni(DTO)_2]I_{1.0}$ must await a single-crystal structural determination, our present conception of the bonding in this molecular metal involves localized magnetic states (molecular orbitals) of comparable energy to a partially-filled band formed by direct overlap of either d_{z^2} or ligand π orbitals on adjacent stacked $Ni(DTO)_2$ units. It is interesting to speculate that the metallic electrical conductivity of $K_2[Ni(DTO)_2]I_{1.0}$ may arise through formation of a band which is a strong admixture of both ligand and metal orbitals and that this strong intrachain bonding gives rise to enhanced stability of the metallic state in this compound.

Acknowledgement: This work was supported in part by the Office of Naval Research.

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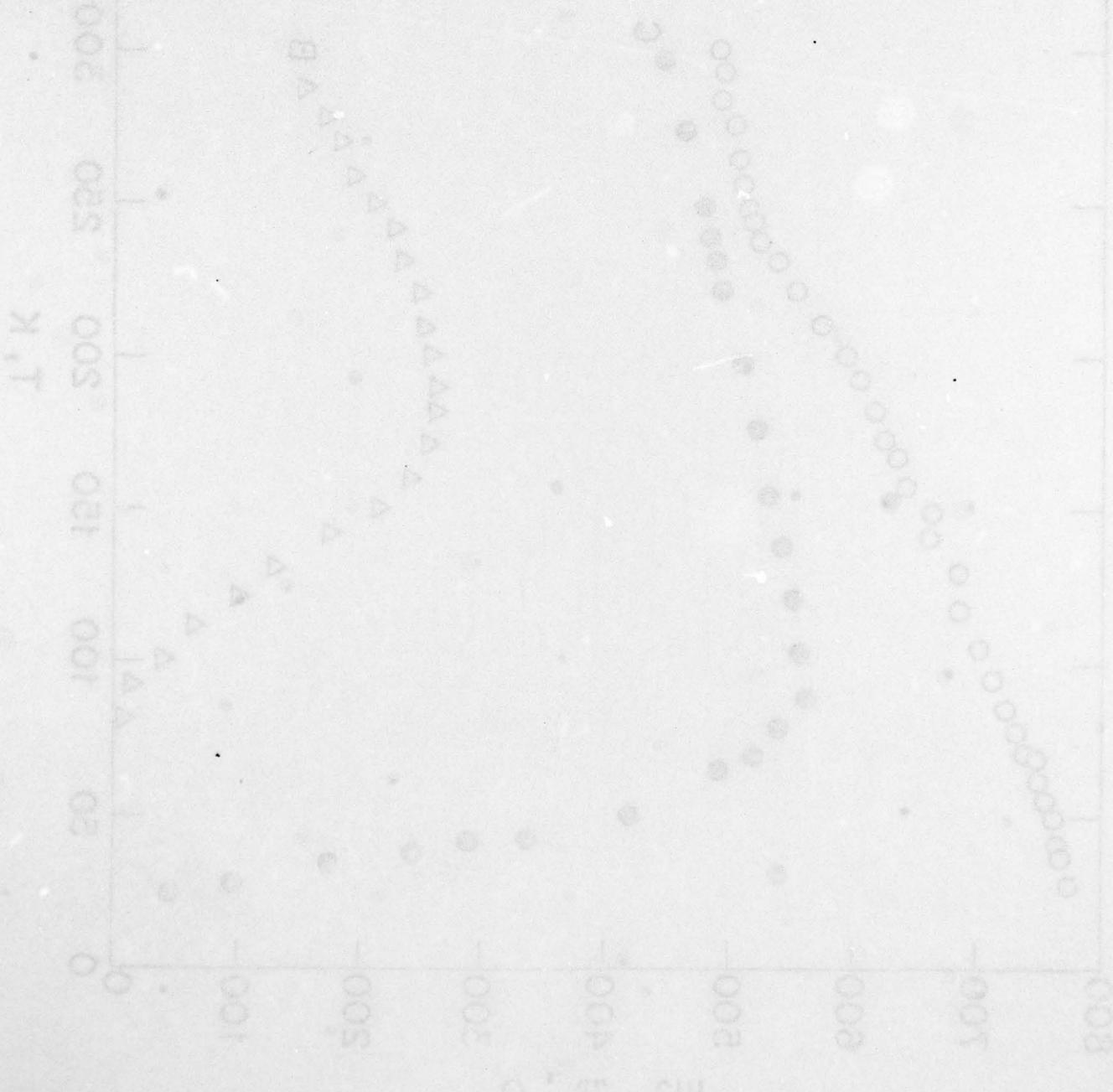
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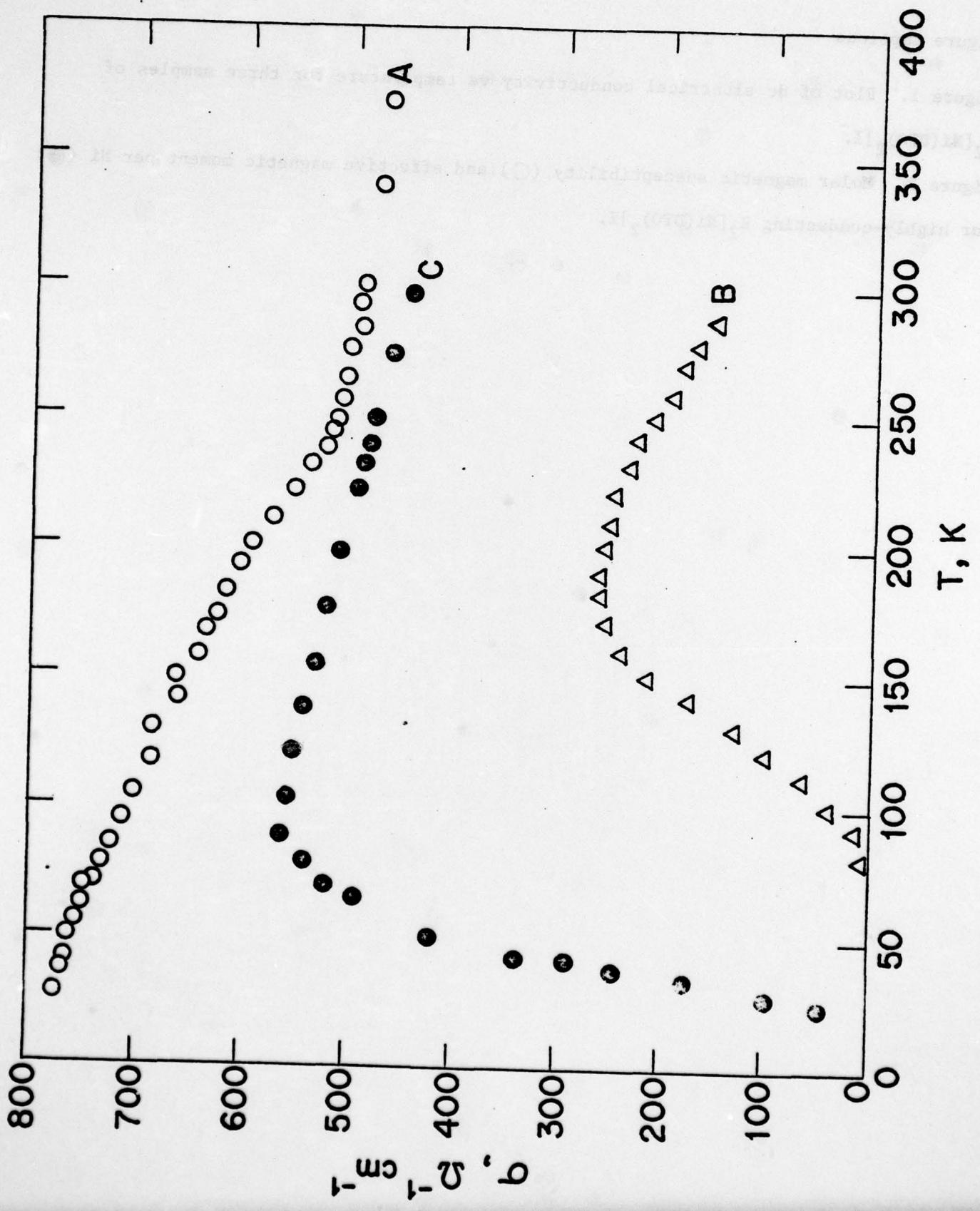
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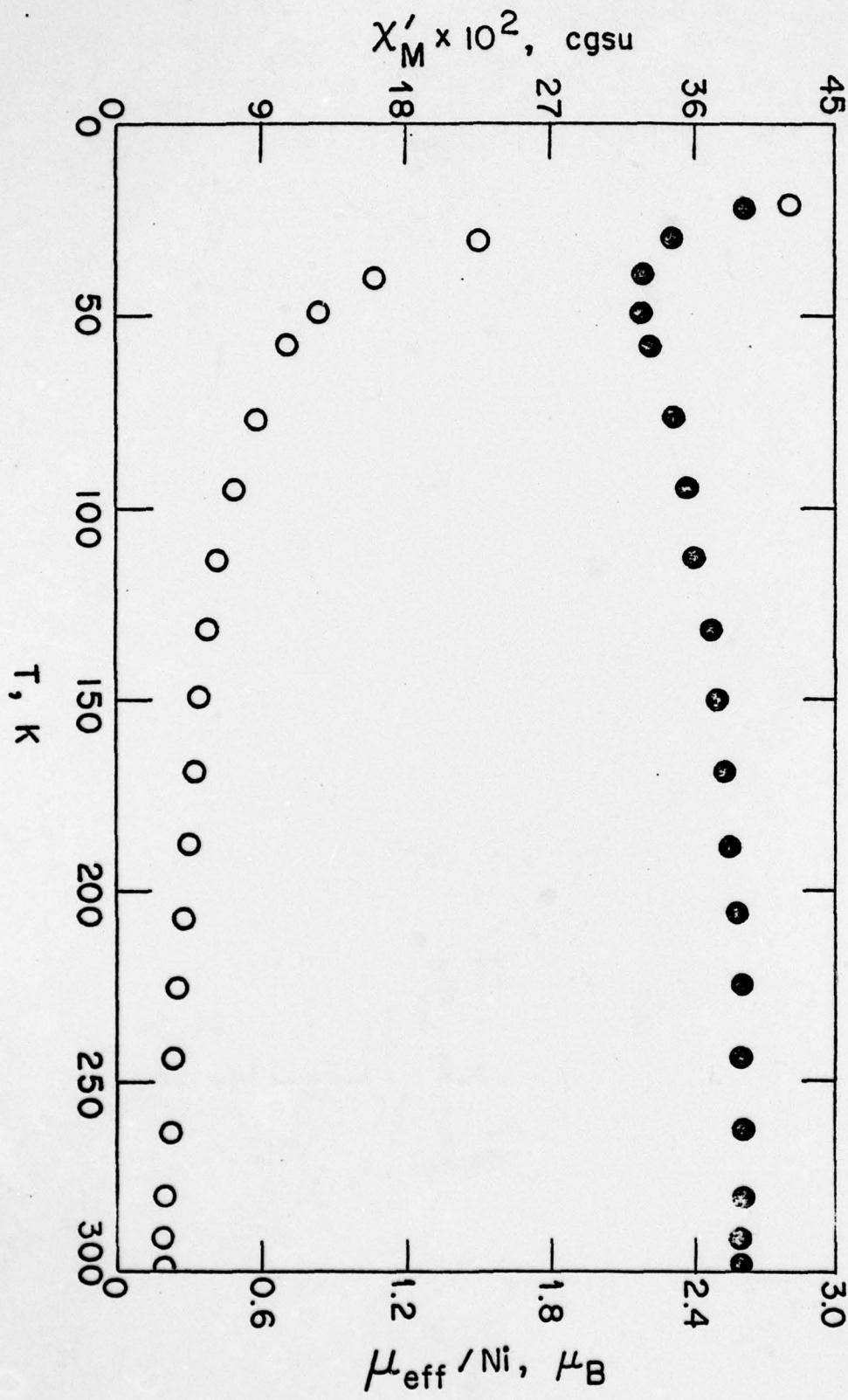
Figure Captions

Figure 1. Plot of dc electrical conductivity vs temperature for three samples of $K_2[Ni(DTO)_2]I$.

Figure 2. Molar magnetic susceptibility (\bigcirc) and effective magnetic moment per Ni (\bullet) for highly-conducting $K_2[Ni(DTO)_2]I$.







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